

Trends in California Gasoline Properties and Motor Vehicle Emissions

Robert Harley

Civil & Environmental Engineering Dept.

University of California at Berkeley

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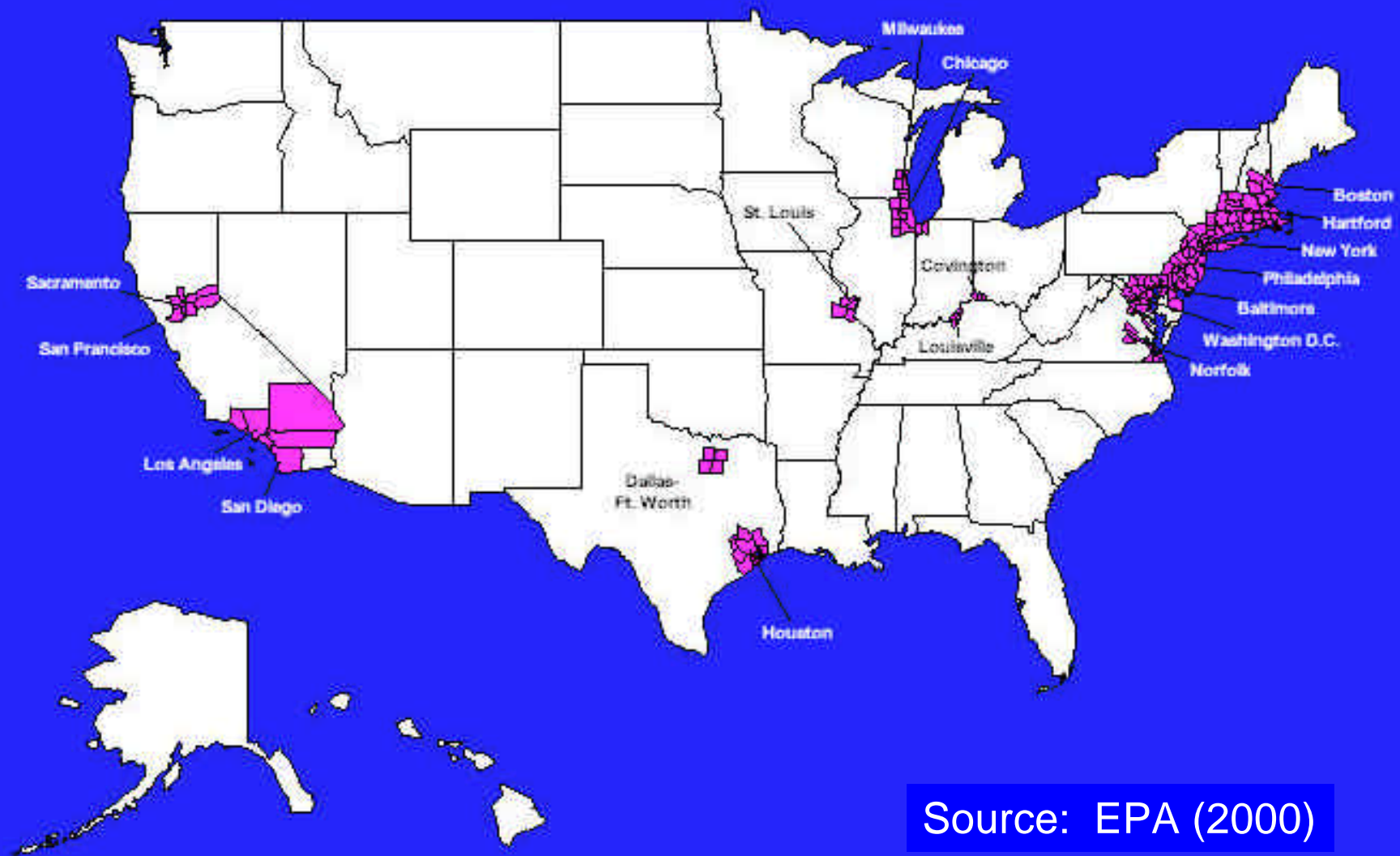
Acknowledgments

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 - California Air Resources Board

Introduction

- Major changes to gasoline since 1990:
 - Wintertime use of oxygenates (1992)
 - California RFG (1992, 1996)
 - Federal RFG (1995, 2000)
- Further changes are underway!
 - MTBE will be phased out in California by end of 2002

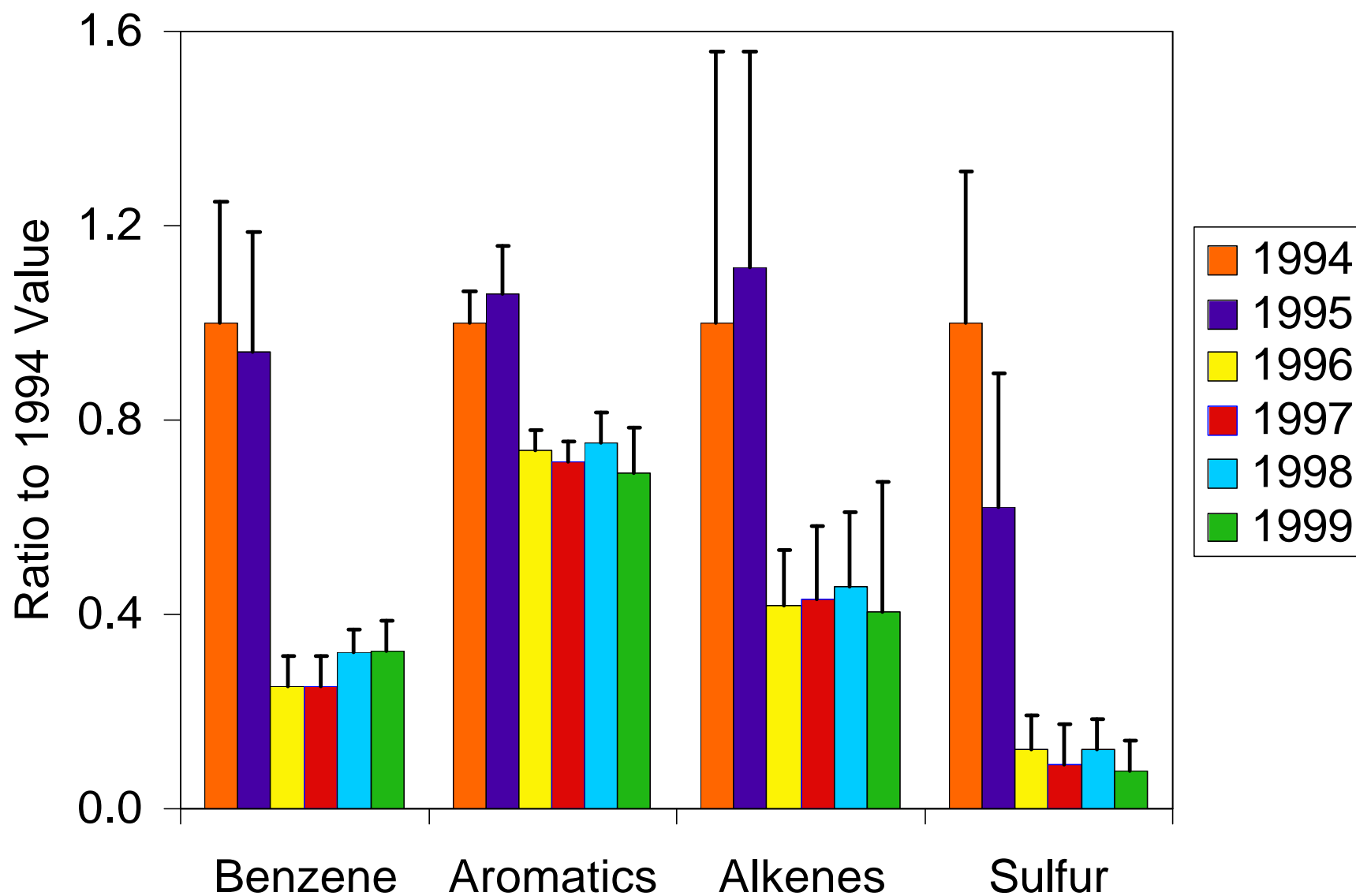
Federal Reformulated Gasoline Areas



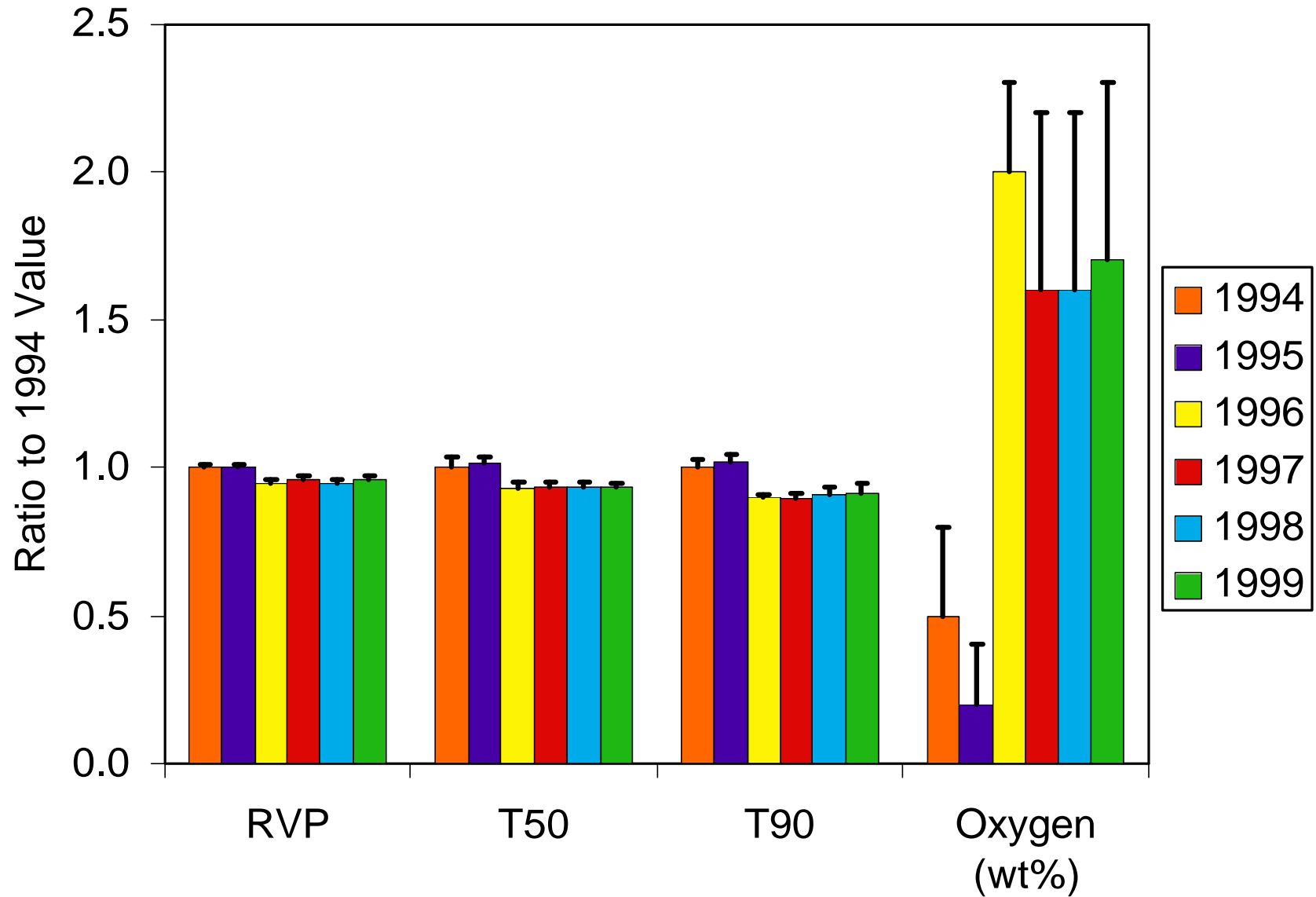
Bay Area Gasoline (1994)

Benzene (vol%)	1.6 ± 0.4	RVP (psi)	7.4 ± 0.1
Aromatics (vol%)	31.9 ± 2.1	T ₅₀ (°F)	214 ± 8
Alkenes (vol%)	7.9 ± 4.4	T ₉₀ (°F)	334 ± 8
Sulfur (ppmw)	131 ± 41	Oxygen (wt%)	0.5 ± 0.3

Bay Area Gasoline Trends



Bay Area Gasoline Trends



Vehicle Emissions

- Most studies of fuel effects have relied on laboratory dynamometer testing
 - Test one vehicle at a time
 - Simulate stop-and-go city driving
 - Repeat using different fuel formulations
- For example, see Auto/Oil study (Hochhauser *et al.*, SAE 912322)

Caldecott Tunnel

- Tunnel on hwy. 24 east of Oakland, CA
 - 1100 meters (0.7 mile) long
 - Three two-lane traffic tubes
 - Sample in middle bore (no diesel trucks)
 - Sample 10 days each summer 1994-99
 - Sample 4-6 PM (>4000 vehicles/hour)
 - Traffic is eastbound/uphill on 4.2% grade



Pollutant Measurements

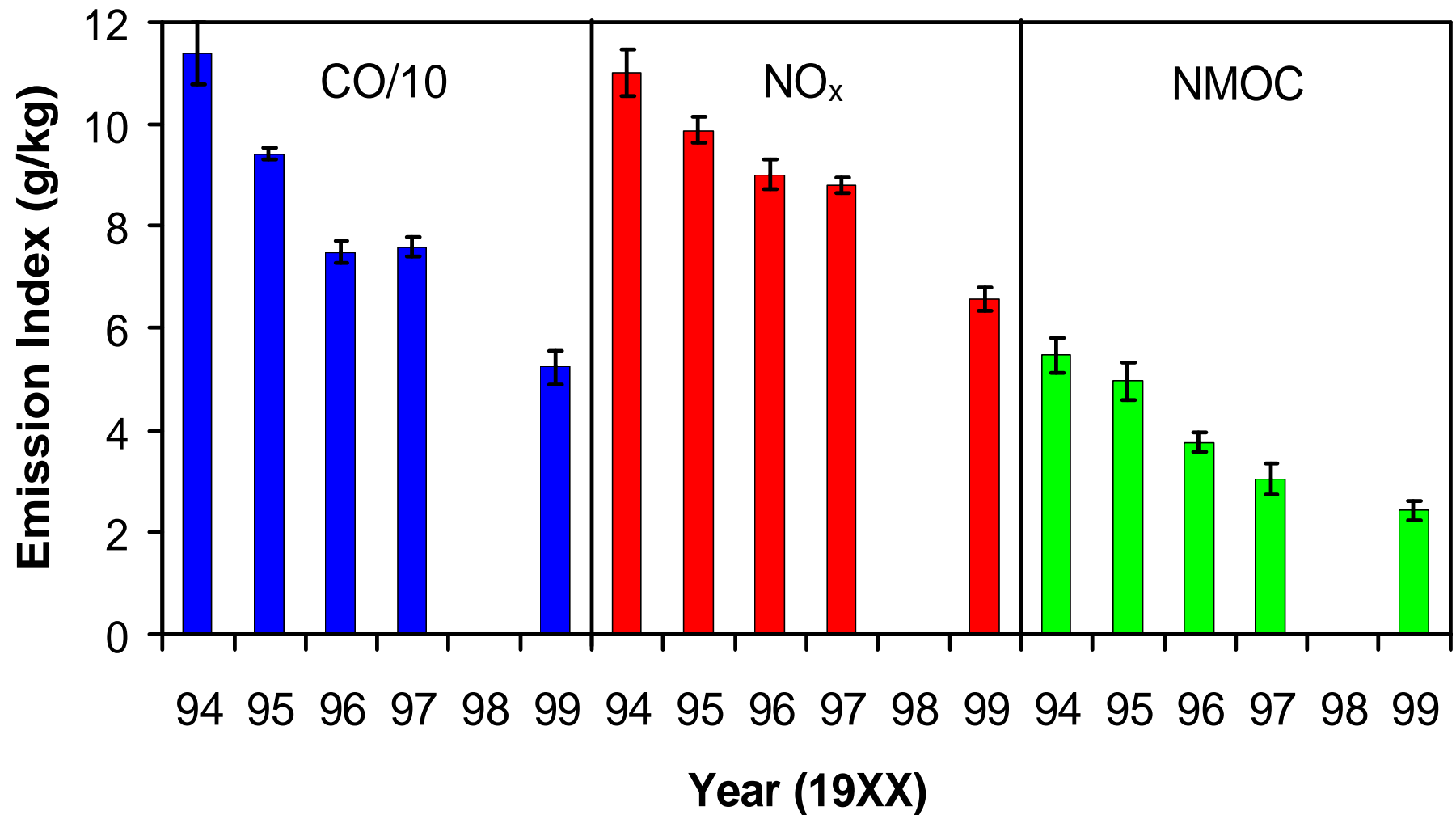
- Carbon dioxide (CO_2)
- Carbon monoxide (CO)
- Nitrogen oxides (NO_x)
- Non-methane hydrocarbons (NMHC)
- Methyl tert-butyl ether (MTBE)
- Methane (CH_4)
- Aldehydes

Pollutant Measurements

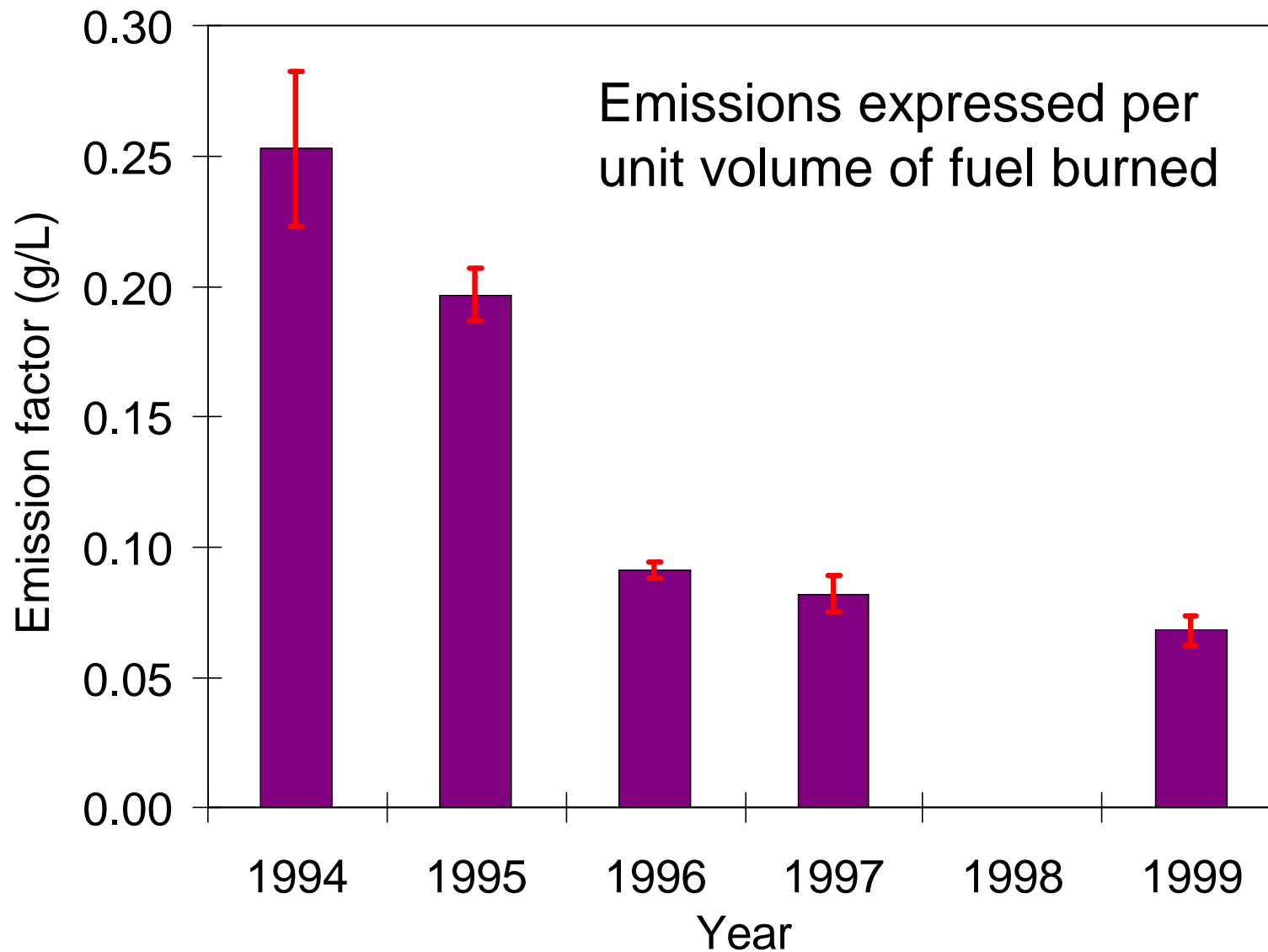


Emission Factor Trends

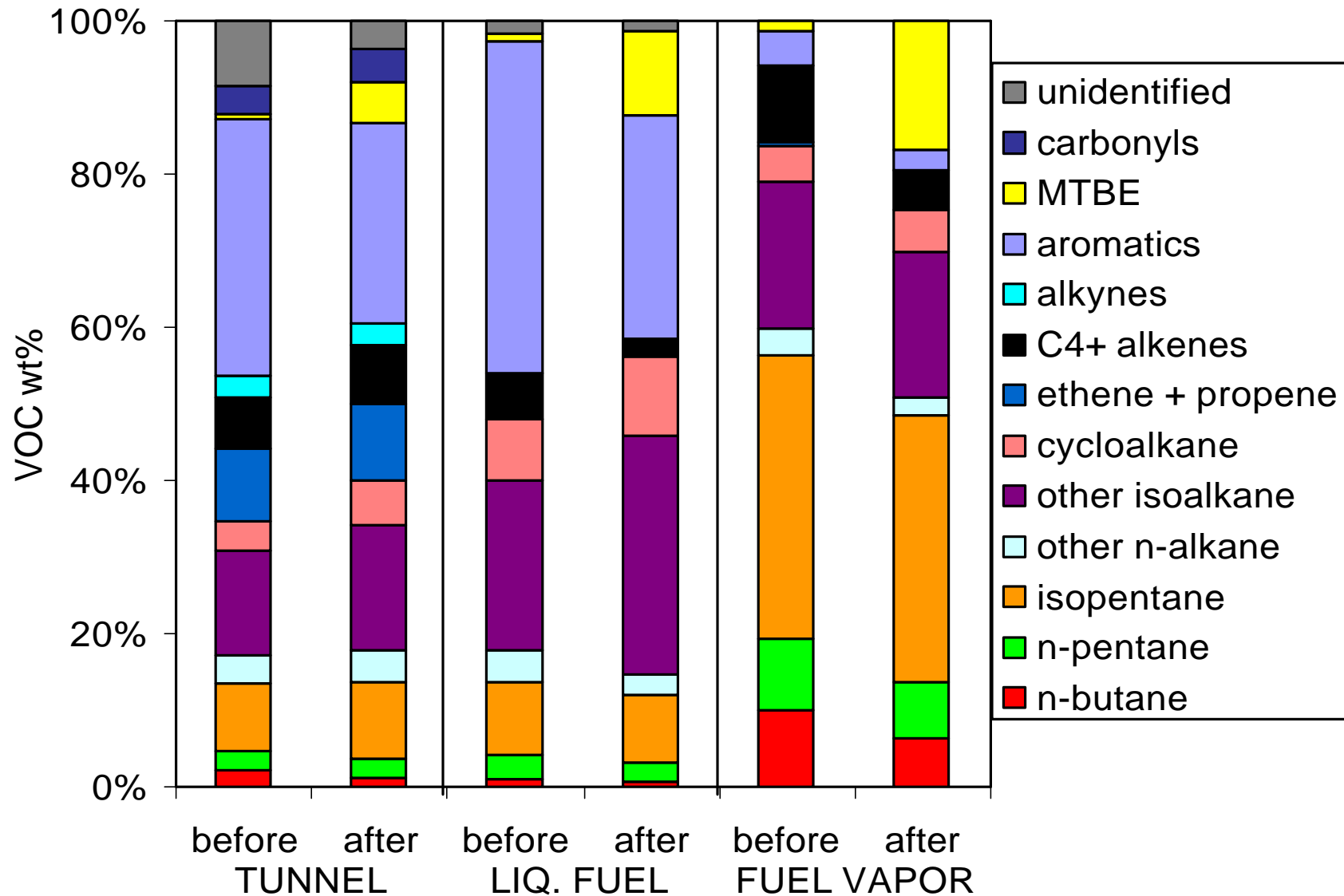
Emissions expressed per unit mass of fuel burned



Benzene Emission Trends



Effects of Fuel Change on VOC

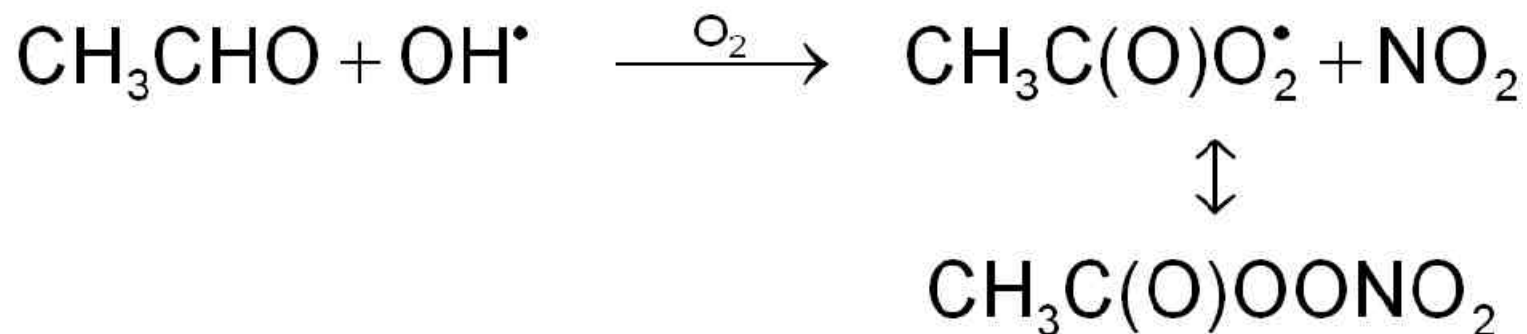


Summary

- Emission factors decreased between 1994 and 1999:
 - Benzene down by $73 \pm 12\%$
 - NMOC down by $55 \pm 7\%$
 - CO down by $54 \pm 6\%$
 - NO_x down by $41 \pm 4\%$
- Improved vehicle technology more important than fuel changes, except benzene where contribution due to fuel changes is 30-40%

Air Quality Issues: Ethanol

- Acetaldehyde (CH_3CHO) emissions will increase by $\sim 150\%$ if ethanol added to gasoline at 10 vol% (SAE 920326)



Peroxyacetyl nitrate (PAN)

Vapor Pressure

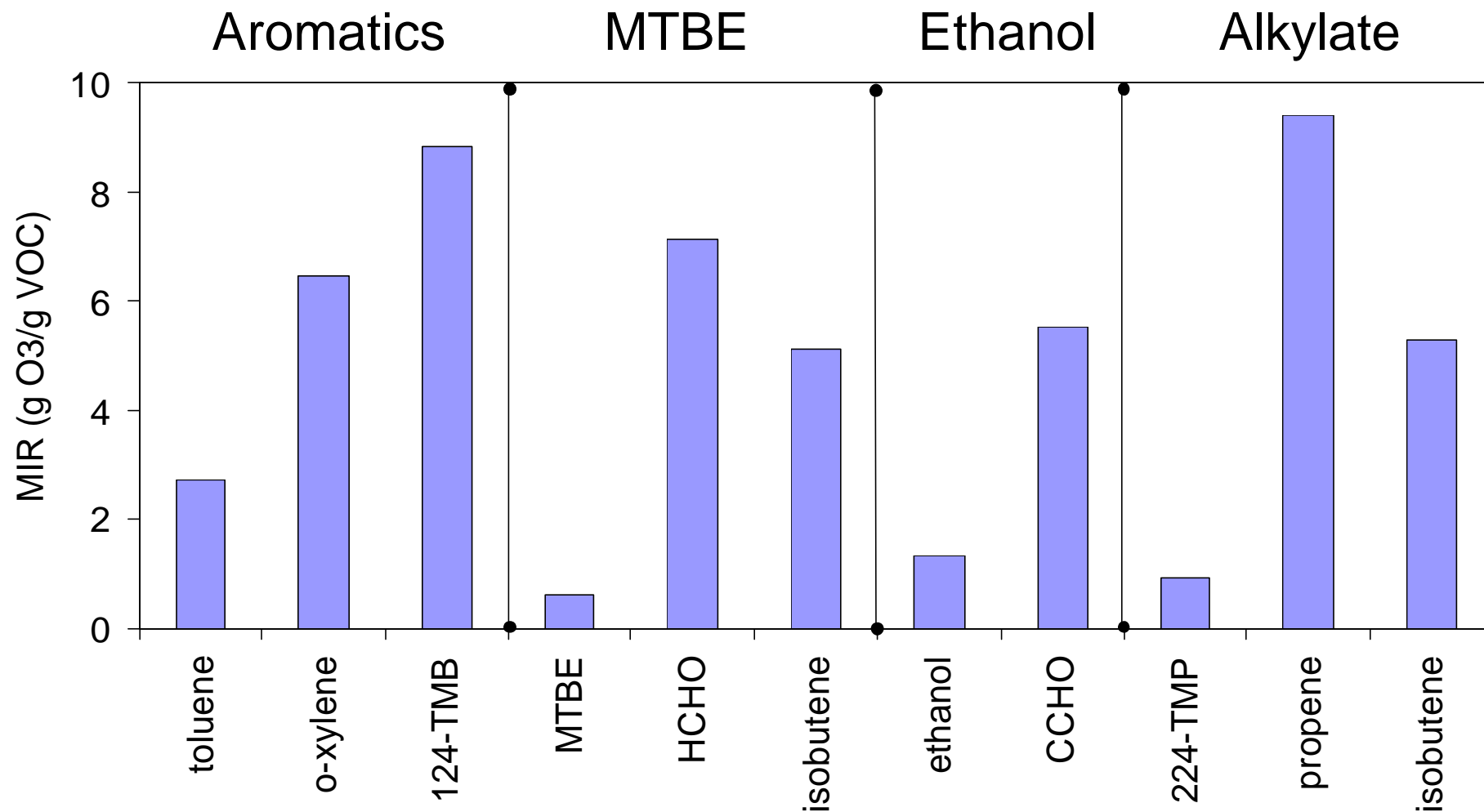
- Affects tendency of gasoline to evaporate in hot weather
- Gasoline v.p. limit 48 kPa at 38°C
- Ethanol has v.p. of 16 kPa at 38°C
- Adding ethanol should lower v.p. of gasoline... right?

No! It forms non-ideal solution and vapor pressure increases.

Air Quality Issues: Alkylate

- Strong acid catalysts (HF, H₂SO₄) used in refinery alkylation process are hazardous
- Alkylate in gasoline is a precursor to emissions of C₃-C₄ alkenes (highly reactive) in vehicle exhaust
- Higher energy content than oxy-fuels

VOC Reactivity



Conclusions

- Reactivity of exhaust VOC with respect to ozone formation is unlikely to change for MTBE vs. ethanol vs. alkylate
- Potential air quality impacts:
 - Vapor pressure problems, increased acetaldehyde & PAN formation (for EtOH)
 - Hazardous strong acid catalysts used in refineries to make alkylate

References:

Environ. Sci. Technol.

- Kirchstetter *et al.*, vol. 33, pp. 318-28, 1999a.
- Kirchstetter *et al.*, vol. 33, pp. 329-36, 1999b.
- Kean *et al.*, vol. 34, pp. 3535-39, 2000.
- Harley *et al.*, vol. 34, pp. 4088-94, 2000.